

A NOVEL TITANIUM COMPLEX WITH LINKED β -DIKETONATO-INDENYL LIGAND FOR CATALYTIC SYNDIOSPECIFIC POLYMERIZATION OF STYRENE*

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Abstract A novel ligand (**3**), in which the indenyl group is linked to a β -diketone moiety through a three-carbon bridge, and its titanium complex (**4**) were synthesized. The titanium complex was employed as a metallocene analog with co-catalyst methylaluminoxane (MAO) in catalytic syndiospecific polymerization of styrene to give highly syndiotactic polystyrene (*s*-PS, 96%–97%). Polymerization temperature (T_p) strongly influenced the catalytic activity and syndiotacticity of the produced PS. The activities of catalyst **4** increase from 1.84×10^6 to 3.26×10^6 gPS/molTi $\cdot$ h with the increase of T_p from 60°C to 80°C and the syndiotacticities of the produced *s*-PS also increase slightly. Then, both the catalytic activity and the syndiotacticity of PS decrease at T_p of 90°C.

Keywords β -Diketone, Metallocene, Syndiospecific polymerization, Polystyrene

INTRODUCTION

The development of a new generation of well-defined coordination complexes has had an enormous impact on the development of new polymerization catalysts and reactions^[1]. Metallocenes are an important class of organometallics with many applications as polymerization catalyst^[2]. As to their unique characteristics, the search for new or modified reactivity prompts the investigation of alternative supporting ligand systems for the metal^[1b]. For example, replacing the dicyclopentadienyl ligand system by a combination of an amide and a cyclopentadienyl ligand to form a half-sandwich complex with metal as the metallocene analogs turns on the catalytic polymerization of propene^[1c]. Similarly, alkoxo-cyclopentadienyl metal complexes were also developed for olefin-polymerization^[3]. A great potential for imparting novel properties to the resulting chelate complexes and for controlling the metal reactivity seems to emerge.

Recently, syndiotactic polystyrene (*s*PS) has attracted considerable attention because of its excellent performance, such as higher thermomechanical properties that are approximately three times greater than those of conventional PS. In 1986, Ishihara *et al.*^[4] reported an active catalyst system for highly syndiospecific polymerization of styrene: cyclopentadienyl titanium with methylaluminoxane (MAO) as cocatalyst, while the analogous of Zr, V, Nb, Cr and Co compounds produced either atactic polystyrene (*a*PS) or none. After that time, a number of studies based on the application of various Ti-complex/ MAO catalyst systems in syndiospecific polymerization of styrene were reported^[5].

In this paper, we wish to report the syntheses of a novel ligand, in which the indenyl group is linked to a β -diketone moiety by a three-carbon bridge $[(CH_2)_3]$, and a corresponding complex with titanium. The structure of

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the titanium complex is similar to that of alkoxo-cyclopentadienyl titanium complex and used as a metallocene analog with co-catalyst MAO in catalytic syndiospecific polymerization of styrene. The effects of polymerization temperature (T_p) on the catalytic activity and syndiotacticity of the produced *s*-PS were also investigated.

EXPERIMENTAL

Measurement

IR spectra were recorded on a Perkin-Elmer-683 infrared spectrophotometer. ^1H -NMR and ^{13}C -NMR spectra were recorded with a Bruker DMX-300 or a Varian Unity-200 spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectrometry (MS) and high-resolution mass spectrometry (HRMS) spectra were obtained from AEI MS-50 mass spectrometer. Elemental analyses were measured with a Flash EA1112 elemental analyzer.

Material

Ether and THF were used after refluxing and distilling over sodium. MAO was purchased from Albemarle Company and TiCl_4 , methanol and styrene were obtained from Beijing Chemical Company. Tetrabutylammonium fluoride (TBAF) was purchased from Acros Company. 3-Indenylpropyl bromide **1** was synthesized according to the literature^[6]. All the reactions for synthesis of the catalyst and polymerization of styrene were carried out under argon atmosphere using standard Schlenk technique.

Synthesis of 3-(3'-indenylpropyl)-2,4-pentanedione **3**^[7]

A solution of pentane-2,4-dione **2** (0.50 g, 5 mmol) in THF (15 mL) was placed in a two-necked round-bottom flask (50 mL) equipped with a magnetic stirrer. TBAF (0.79 g, 2.5 mmol) was added and the mixture was stirred for 5 min. On heating this mixture at 80–90°C under reduced pressure, the solvents were rapidly evaporated to obtain an anhydrous residue. The residue was washed with cold ether and then dissolved in chloroform (10 mL). **1** (0.59 g, 2.5 mmol) was added and the mixture was stirred at room temperature for 2 h, then at 80°C for 4 h. After cooling to room temperature, the mixture was diluted with ether (25 mL), filtered, and evaporated. The residue obtained was purified by flash chromatography (silica gel, ethyl acetate: petroleum ether = 1:20) to afford the C-alkylation product, **3**, 0.29 g (45%). IR (neat): 2930, 1690, 1355, 770 cm^{-1} ; ^1H -NMR (CDCl_3 , δ): 7.17–7.47 (4H, m), 6.23 (1H, t, J = 1.8 Hz), 3.66 (1H, t, J = 7.2 Hz), 3.34 (2H, bs), 2.56 (2H, t, J = 7.4 Hz), 2.14 (6H, s), 1.97 (1H, q) and 1.65 (1H, q). ^{13}C -NMR (δ): for keto form **3a**: 191.1, 145.1, 144.4, 143.4, 131.3, 128.0, 126.0, 124.7, 123.8, 118.8, 68.8, 37.3, 28.8, 25.8, 22.9; for enol form **3b**: 204.4, 145.2, 144.4, 143.8, 131.3, 128.2, 126.6, 124.8, 123.8, 118.8, 110.3, 37.7, 29.1, 28.1, 27.5, 25.8, 22.9. m/z : 256(M^+), 238, 195, 155, 141, 115, 128, 43 (100); HRMS: Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}$ ($\text{M}-\text{H}_2\text{O}$): 238.1353, Found: 238.1352.

Preparation of Titanium Complex **4**

A solution of **3** (0.8 g, 2.5 mmol) in ether (30 mL) was placed in a 100 mL two-necked round-bottom flask equipped with a magnetic stirrer. *n*-Butyllithium in hexane solution (1.6 mol/L, 38 mL) was added dropwise under nitrogen at -78°C . The mixture was stirred at -78°C for 3 h, and then at room temperature overnight. Solvent was evaporated and the residue was washed several times with pentane. The corresponding dilithium salt was obtained after drying the residue in vacuum at 70°C for 10 h. 30 mL THF was added and cooled to -78°C . Titanium chloride (5.0 mmol) was added within 1 h. Then the reaction temperature was slowly warmed to room temperature. After stirring for 36 h, the precipitate was filtered off and the filtrate was concentrated and the metal complex was obtained after cooling. Pure product **4** (1.9 g, 23%) was obtained as a yellow solid after recrystallization from benzene-pentane. ^1H -NMR (CDCl_3 , δ): 7.23–7.42 (4H, m), 7.38 (1H, d, J = 6.8 Hz), 6.26 (1H, d, J = 8.9 Hz), 3.67 (2H, m), 2.34 (3H, s), 2.10 (3H, s), 1.60–1.89 (2H, m), 1.25–1.44 (4H, m). EA: Calcd for $\text{C}_{17}\text{H}_{18}\text{TiCl}_2\text{O}_2$ (%): Ti, 12.87 Found: 12.08. m/z : 338 (M^+-Cl), 253 (M^+-TiCl_2), 239 ($\text{M}^+-\text{OTiCl}_2$).

Polymerization of Styrene

A glass reactor was charged with 25 mL styrene and a given amount of MAO. Polymerization was initiated upon adding a given amount of titanium catalyst (Table 1). After stirring for 30 min, the reaction mixture was

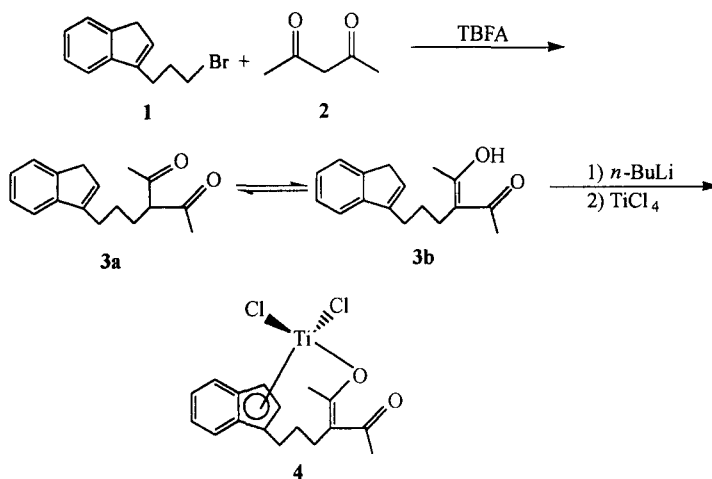
quenched by adding methanol. The polymer was precipitated with 3% hydrochloric acid in methanol, washed with methanol (50 mL $\times$ 3) and dried in vacuum to constant weight.

The total polymer (t-PS) is mainly composed of *s*-PS with a small amount of *a*-PS. As reported by Chien and Salajka^[8], the *a*-PS could be isolated by extracting t-PS with boiling 2-butanone for 3 h. Syndiotacticity of the produced polystyrenes is expressed as the percentage of material insoluble in boiling 2-butanone (equal to the yields of *s*-PS).

RESULTS AND DISCUSSION

Synthesis of the Ligand Compound and the Titanium Complex

It is well known that 3-substituted 2,4-pentanedione can be synthesized by alkylation of 2,4-pentanedione **2** with alkyl halides under basic condition^[9]. However the alkylation reactions always give a mixture of C— and O—alkylation products. It was reported^[10] that the reactions of **2** with alkyl iodides in the presence of TBAF are regioselective C-alkylations. Based on this method, **3** was prepared. The ligand **3** is a mixture of keto form **3a** and enol form **3b** (**3a**:**3b** = 4:1) with 45% yield. Subsequently, **3b** reacted with TiCl₄ to give the titanium complex **4** in 23% yield (Scheme 1). In the course of the reaction, **3a** could transform into **3b** due to a equilibrium between **3a** and **3b**. Compared with **3**, the ¹H-NMR signals of the titanium complex **4** show some down-field shifts (Table 1), which is attributed to the coordination of titanium with the indenyl moiety, forming a type of alkoxo-cyclopentadienyl ligand titanium complex. In contrast, the molecule of the titanium complex **4** contains the enol form of β -diketone. It is interesting to investigate its catalytic activity in olefin-polymerization.



Scheme 1

Table 1. The ¹H-NMR signals of **3** and **4** (δ)

Compound	Indenyl proton	Methylene proton	Methyl proton
3	6.23 (t), 3.34 (bs)	2.56 (t)	2.14 (s)
4	7.38 (d), 6.26 (d)	3.47 (m)	2.34 (s), 2.10 (s)

When the titanium complex **4** was employed in the polymerization of styrene with a co-catalyst MAO, syndiotactic polystyrene *s*-PS was produced with high catalytic activities (Table 2). From Table 2, it can be found that the catalytic activity of the catalyst **4** is 1.84×10^6 – 3.26×10^6 gPS/molTi $\cdot$ h, which is as high as that of the metallocene catalyst and is noticeably higher than that of β -diketone titanium catalyst (1.72×10^5 – 2.60×10^5 gPS/molTi $\cdot$ h)^[11]. The syndiotacticity of the produced PS is as high as 96.2%–97.5%. As reported^[4], the most important resonances of ¹³C-NMR for characterizing *s*-PS are methylene, methenyl and phenyl C-1 carbon signals. It was found in the ¹³C-NMR spectrum of the produced PS (Fig. 1) that methylene carbon (CH₂) at δ = 44.6, methenyl carbon (CH) at δ = 41.3 and phenyl C-1 carbon at δ = 145.7 can be assigned to the carbon

resonance of the syndiotactic stereosequence^[10].

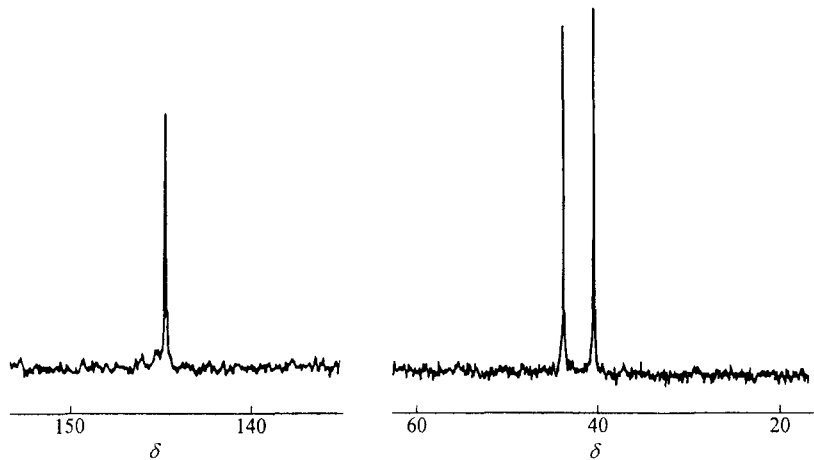


Fig. 1 ¹³C-NMR spectrum of the produced PS

Table 2. Effects of *T_p* on catalyst activity of **4** and syndiotacticity of PS

<i>T_p</i> (°C)	Yield (gPS)	Activity (× 10 ⁶ gPS/molTi · h)	Syndiotacticity (%)
90	15.6	3.11	97.1
80	16.3	3.26	97.5
70	15.1	3.02	96.7
60	9.2	1.84	96.2

Polymerization conditions: MAO/Ti = 800:1 (mol/mol), [Cat]=10 μmol, Styrene: 30 ml., polymerization time: 30 min

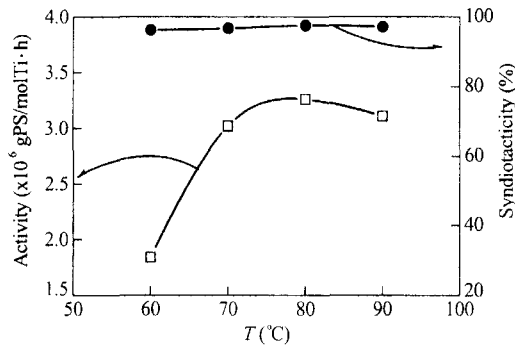


Fig. 2 Effects of *T_p* on activity of **4** and syndiotacticity of PS

The effects of polymerization temperature (*T_p*) on the catalyst activities and the syndiotacticities were examined (Table 2, Fig. 2). It is shown in Table 2 that the activities of catalyst **4** increase from 1.84×10^6 to 3.26×10^6 gPS/molTi · h with the increase of *T_p* from 60°C to 80°C and the syndiotacticities of the produced *s*-PS also increase slightly. Then, both the activity of the titanium catalyst **4** and the syndiotacticity of the PS decrease at *T_p* of 90 °C, which could be attributed to the decomposition and deactivation of the titanium complexes at higher temperature and the irregular insertion in the chain propagation step^[12]. Further investigation of the catalyst in olefin polymerization is in progress.

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